

Electrochemical treatment of bisphenol-A using response surface methodology

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Received: 5 October 2011 / Accepted: 27 December 2011 / Published online: 5 January 2012
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Abstract The decomposition of bisphenol-A (BPA) in synthetic solution and in municipal effluent was investigated using an electro-oxidation process. Electrolysis was conducted using a cylindrical electrolytic cell containing two circular anodes (expanded metal) and two circular cathodes (stainless steel) alternated in the electrode pack. Different anode materials (Ti/SnO₂, Ti/IrO₂ and Ti/PbO₂) were tested, and Ti/PbO₂ was found to be the most effective electrode for BPA degradation. An experimental design methodology (2³ Box–Behnken design) was applied to determine the optimal experimental conditions in terms of cost effectiveness. The BPA concentration ($C_0 = 1.0 \text{ mg l}^{-1}$) could be optimally diminished by up to 90% by applying a current intensity of 2.0 A for a 100-min reaction period in the presence of $250 \text{ mg Na}_2\text{SO}_4 \text{ l}^{-1}$ (used as a supporting electrolyte). Then, the optimal conditions were applied on a municipal wastewater effluent (sampled after secondary treatment) artificially contaminated with 1 mg BPA l^{-1} without the addition of a supporting electrolyte. The treatment was more effective with the municipal effluent due to the presence of a high concentration of chloride ions that could easily be transformed into active chlorine. BPA could be oxidized by both direct anodic electrochemical oxidation (by means of OH·) and indirect electrochemical oxidation via mediators, such as hypochlorous acid generated by chloride oxidation. Both actions (direct and indirect effects) lead to the formation of powerful oxidizing agents capable of rapidly oxidizing BPA.

Keywords Bisphenol-A · Electro-oxidation · SnO₂/Ti · IrO₂/Ti · PbO₂/Ti · Response surface methodology · Power consumption

Abbreviations

AHH	Aliphatic halogenated hydrocarbon
AMH	Aromatic monocyclic hydrocarbon
AOP	Advanced oxidation process
BBD	Box–Behnken experimental design
BDD	Boron-doped diamond
BPA	Bisphenol-A
COD	Chemical oxygen demand
DSA	Dimensionally stable anode
MWE	Municipal wastewater effluent
ORP	Oxidation-reduction potential
RSM	Response surface methodology
THM	Trihalomethane
WTP	Wastewater treatment plant

1 Introduction

Bisphenol-A (BPA) is an anthropogenic organic substance widely used around the world for the production of polycarbonate plastics, epoxy resins and acrylic glass. BPA is a refractory compound that is found in surface and ground water and in sediment. BPA concentrations detected in the wastewater treatment plant effluent are in the range of $0.16\text{--}0.36 \text{ } \mu\text{g l}^{-1}$ [1]. According to our knowledge, the maximum concentration of BPA detected was 17.2 mg l^{-1} in waste landfill leachates [2]. Recent works demonstrated that the low concentrations of BPA (even below $1 \text{ } \mu\text{g l}^{-1}$) in aquatic ecosystems had adverse effects [3, 4]. Table 1

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shows some important characteristics of BPA. Due to its endocrine-disrupting properties, BPA is suspected to represent a danger for a wide range of living organisms. BPA cannot be efficiently treated by conventional water treatment processes and thus can be found in drinking water [5, 6]. To treat efficiently BPA in wastewater or natural water (surface or ground water), a new type of treatment corresponding to advanced oxidation processes (AOPs) has been investigated. All of these processes are based on hydroxyl radical production, which is a powerful oxidant able to react efficiently and non-selectively with several types of refractory organic pollutants such as BPA [7, 8]. Among these different AOPs, electro-oxidation is interesting due to its “green” aspect in using electricity, its flexibility and its capacity to react with pollutants by both the direct and indirect effects of electricity. Direct oxidation may be achieved through mineralization with hydroxyl radical ($\text{OH}\cdot$) produced by DSAs (dimensionally stable anodes) with high oxygen overvoltages, such as SnO_2 , PbO_2 and IrO_2 [9–11]. In fact, $\text{OH}\cdot$ radicals are exclusively generated on anodes from the oxidation of water, and organic compounds can be completely transformed or degraded by reaction with adsorbed $\text{OH}\cdot$ radicals. Indirect oxidation can be achieved through the electrochemical generation of a mediator in solution (such as HClO , HBrO , H_2O_2 , $\text{H}_2\text{S}_2\text{O}_8$, and others) to convert toxic organics to less harmful products by using graphite or noble-metal anodes [12–14]. This type of technology has been widely applied using different electrode materials for the treatment of various effluents containing refractory organic compounds, including textile effluents [15], landfill leachate [16, 17], olive oil wastewater, domestic sewage sludge [18], and tannery effluent [19, 20]. Numerous authors have investigated the efficiency of electro-oxidation of BPA on different anode materials such Ti/BDD , Ti/Sb-SnO_2 , Ti/RuO_2 , Ti/SnO_2 , Ti/PbO_2 and Ti/Pt [6, 21, 22]. However, all of these studies have been performed using a synthetic effluent with a maximum volume of 100 ml.

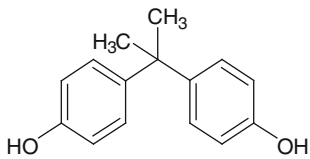
In this present study, the electrochemical oxidation of BPA was investigated using three types of circular anodes, Ti/PbO_2 , Ti/IrO_2 and Ti/SnO_2 , in an electrolytic system with a working volume of 3.5 l. The first part of this work evaluated the behavior of each electrode in the presence of BPA solution using cyclic voltamperometry and chronopotentiometry. Subsequently, preliminary galvanostatic electrolysis tests were conducted to define the experimental region for the response surface methodology (RSM). The second part concerns the use of a statistical methodology for the rational analysis of the combination of operational factors that led to the best treatment of the electro-oxidation process for BPA removal. A Box–Behnken experimental design (BBD) was used to optimize BPA degradation in terms of cost effectiveness. The third part of this study involved applying the optimal conditions from the experimental design to a real municipal effluent contaminated by BPA and evaluating the toxicity of the treated effluent by measuring aromatic monocyclic hydrocarbons (AMH) and halogenated hydrocarbon by-products.

2 Materials and methods

2.1 Cyclic voltammetric study

A preliminary voltammetric study was performed with a three-electrode Voltalab 80 system (Radiometer analytical) equipped with a rotating working electrode (CVT 101, Radiometer analytical). It included a potentiostat/galvanostat (Tacussel 20 V/1A PGP 201). The reference electrode was a saturated calomel ($\text{Hg/Hg}_2\text{Cl}_2/\text{KCl}$) electrode (Tacussel XM 110), while the auxiliary electrode was platinum (Taccusel Pt XM 140). The materials used as the working electrodes were titanium coated with lead oxide (Ti/PbO_2 , 11 mm diameter), titanium coated with iridium oxide (Ti/IrO_2 , 11 mm diameter) and titanium coated with tin oxide (Ti/SnO_2 , 11 mm diameter). Cyclic voltammetric

Table 1 Characteristics of the BPA

Parameters	Units	Bisphenol-A (BPA)
Molecular structure		
		
Formula		$\text{C}_{15}\text{H}_{16}\text{O}_2$
MW ^a	(g mol^{-1})	228.29
Density	(g ml^{-1})	1.2
Solubility in water	(mg l^{-1})	300
pK (25 °C)	–	9.6–11.3

^a Molecular weight

and chronopotentiometric measurements were conducted in a 0.1 M Na_2SO_4 electrolyte solution in the presence of 200 mg BPA l^{-1} .

2.2 Preparation of the synthetic solution

Analytical grade BPA (purity >99%) was acquired from Sigma-Aldrich. A stock solution of BPA ($1.75 \text{ g BPA l}^{-1}$) was prepared in a methanol solution (purity 99.9%). Then, 2 and 20 ml of the stock solution of BPA were, respectively, added to 3.5 l of distilled water. The conditioning step was performed at a high speed of 750 rpm for 20 min. Mixing was achieved by using a Teflon-covered stirring bar placed at the bottom of the beaker. The resulting mixture constituted the synthetic BPA [final concentrations of 1 and 10 mg l^{-1} (BPA), respectively, and 0.06% and 0.6% of methanol, respectively] in which Na_2SO_4 was added at a concentration varying from 150 to 250 mg l^{-1} to increase the conductivity.

2.3 Wastewater BPA-spiking

To test the electro-oxidation process on real effluents containing refractory organic pollutants (refractory COD) and to simulate BPA contamination, wastewater samples were enriched with BPA (1 mg l^{-1}). The effluents were supplied by the Quebec Urban Community wastewater treatment plant (WTP, Québec, Canada). The effluents were sampled at the outlet of a biofiltration unit. The unit is a conventional WTP with a physicochemical pre-treatment and biofiltration treatment system. The treated effluent had an initial content of soluble chemical oxygen demand (COD_s) = $70 \pm 17 \text{ mg l}^{-1}$, $\text{pH} = 7.74 \pm 0.13$, and $\text{TSS} = 18 \pm 5 \text{ mg l}^{-1}$. Samples were collected and stored in polypropylene bottles at 4°C until use. A mixing and stirring time of 10 min was required to completely dissolve BPA prior to electrochemical treatment.

2.4 Electrolytic reactor setup

The reactor unit used in the present work had a 2.0 l capacity, and it was 15 cm (height) \times 14 cm (diameter) and made of PVC material. The electrolytic cell included two anodes and two cathodes in the form of expanded metal, each with a solid surface area of 65 cm^2 and a void surface area of 45 cm^2 . The electrodes were circular disks (12 cm in diameter \times 0.1 cm thick), and titanium (Ti) was used as the cathode. The circular anodes (12 cm in diameter \times 0.1 cm thick) were titanium coated with iridium oxide (Ti/IrO_2), titanium coated with tin oxide (Ti/SnO_2) and titanium coated with lead oxide (Ti/PbO_2), respectively. The inter-electrode gap was 10 mm in the three electrolytic cells. The electrodes were horizontally

installed inside the electrolytic cell, and each anode was placed adjacent to a cathode. The electrodes were supplied by Electrolytica, Inc. (Amherst, NY, USA).

2.5 Experimental unit

The assays were conducted in a closed loop, as depicted schematically in Fig. 1. A 1 l of PVC reservoir (4), a recycling pump (5), and the electrolytic cell (1) constituted the loop. The first assays were conducted in batch recirculation mode with a flow of wastewater entering the bottom of the cell. The recycle flow rate was set at 2.0 l min^{-1} and measured using a flow-meter (6). A needle valve (2) installed before a manometer (3) allowed control over the hydrostatic pressure inside the cell. The excess gas generated during electrolysis was rejected out of the system by means of a venting pipe (11) fixed to the 1 l PVC reservoir. At the start of each assay, raw effluent was injected into the experimental unit by means of a funnel (7) installed in the pipe and connected to the recycling pump, which allowed adding a working volume of 3.5 l. In fact, the electrolytic cell alone had 2.0-l capacity and a 1.0 l of PVC reservoir was connected to the cell. A volume of 0.5 l of water was occupied by the pipe. So, the experimental unit had a total working volume of 3.5 l. The electrochemical cells were operated under galvanostatic conditions, with current intensities (1.0–3.0 A) applied during a period of treatment ranging from 10 to 100 min. The current intensities were applied by means of a DC power source, Xantrex XFR40-70 (Aca Tmetrix, Mississauga, ON, Canada) with a maximum current rating of 70 A at an open-circuit potential of 40 V. During the experiments, the pH and ORP were monitored but not controlled.

2.6 Experimental design

The experimental design of the electro-oxidation process for BPA degradation was implemented using a Box–Behnken design (BBD). Box and Behnken [23] developed a family of efficient three-level designs for fitting second-order response surface methodologies. The methodology of the design is interesting and quite creative. The class of design is based on the construction of balanced incomplete block designs. In the BBD, each pair of factors is linked in a 2^2 factorial (scaling ± 1), while the other ones remain fixed at the center of the experimental region investigated. The last row in the design matrix implies a vector of the center runs. The number of assays required can be calculated as follows: $2^2 \times n \times (n - 1)/2$, where n is the number of variables. In the present study, three variables were considered, and two variables were paired together in 2^2 . In addition, five replicates at the center of the experimental region were required. Thus, the total number of

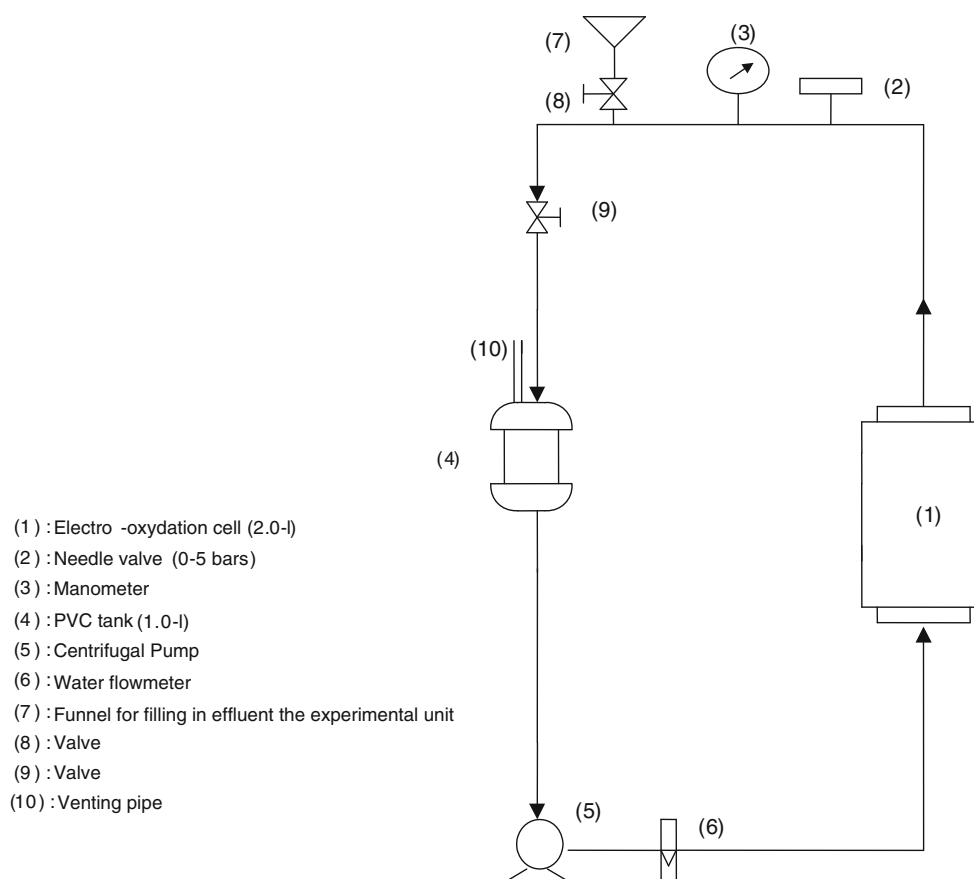


Fig. 1 Schematic view of the electro-oxidation cell with a recirculation loop

assays employed for response surface modeling was 17. The independent process variables used in this study were the applied current intensity (X_1), application time (X_2) and sodium sulfate concentration (X_3). BPA degradation efficiency (Y_1) and energy consumption (Y_2) were considered dependent factors (responses). The values of the process variables and their variation limits were selected based on the preliminary experiments described below in the “Sect. 3”. The experimental region investigated for BPA degradation and the code values are shown in Table 2. The experimental data were analyzed using Design-Expert 7.1 program software including ANOVA to determine the interactions between the process variables and to evaluate the accuracy/correctness of the mathematical model.

2.7 Analytical details

2.7.1 Operating parameters

Values of ORP and pH were determined using an Accumet AR 25 model (Fisher Scientific Ltd, Ontario) model pH meter. The pH and ORP electrodes were silver/silver chloride (Ag/AgCl) and platinum, respectively. A

conductivity meter (Oakton Model 510) was used to determine the ionic conductivity of the effluent.

2.7.2 Extraction and analysis of BPA

The progress of the electrochemical degradation of BPA was monitored after extraction and purification on a solid phase using polypropylene cartridges (Sep-Pak plus C18-cartridges, Waters Inc., ON, Canada). The Sep-Pak-C18 cartridge was successively conditioned by rinsing with 15 ml of methanol (99.9% ACS reagent, EMD chemicals Inc., USA) and 15 ml of distilled water. Subsequently, 20 ml of sample (synthetic BPA solution) was loaded onto the cartridge where it was entirely drip filtered. The non-polar molecules (including BPA and its derivative compounds) retained on the polypropylene cartridge were then eluted with 8 ml of a mixture composed of methanol and dichloromethane (9:1 v/v) (99.8% reagent, LC-MS quality, Fisher Scientific, Canada). After elution, the sample was subjected to evaporation using a heating block at 40 °C under nitrogen (N_2) atmosphere until 2.0 ml (precisely) of residual sample was recovered. The resulting final sample (concentration factor of 10) was then encapsulated in a

Table 2 Preliminary electro-oxidation tests to define the experimental region for response surface methodology (RSM)

Parameters	Anodic electrodes		
	Ti/SnO ₂	Ti/IrO ₂	Ti/PbO ₂
Final pH			7.65
Final temperature (°C)	30.0	26.2	26.4
Initial potential (V)	21.9	16.1	16.3
Final potential (V)	35.7	15.8	16.1
Energy (kW h m ⁻³)	11.5	6.08	6.17
Residual BPA (mg l ⁻¹)	9.2	8.1	3.5
BPA removal (%)	8.0	19	65

$I = 2.0$ A, treatment time = 40 min, $[BPA]_0 = 10$ mg l⁻¹

glass vial (2.0 ml) awaiting analysis using liquid chromatography mass spectrometer (LC–MS).

BPA by-products were analyzed by a Perkin Elmer 500 gas chromatograph (GC) on a VF-5MS-FS column (0.25 mm in diameter, 30 m long and 0.25- μ m film thickness) coupled to a Hewlett-Packard 5973A series mass spectrometer detector operated with a mass range between m/z 50 and 450.

2.8 Economic aspect

The economic study included the consideration of chemical and energy consumption. The electric cost was estimated to be approximately 0.06 US\$ kW h⁻¹. The unit cost of the electrolyte (Na₂SO₄ industrial grade) was 0.30 US\$ kg⁻¹. The total cost was evaluated in terms of US dollars spent per cubic meter of treated solution (US\$ m⁻³).

3 Results and discussion

3.1 Electrochemical behavior of bisphenol-A on different anodes

It is well known that the type of anode material used can greatly influence electrochemical oxidation processes [8–10]. This can be attributed to the different crystalline natures of electrodes that catalyze electrochemical oxidation [24, 25]. Thus, prior to performing a galvanostatic study, cyclic voltammetric (CV) and chronopotentiometric (CP) investigations were conducted to determine the oxidation behavior of BPA on Ti/SnO₂, Ti/IrO₂ and Ti/PbO₂ anodes, respectively, at a sweep rate of 150 mV s⁻¹. According to the CV curves (Fig. 2), the oxidation peak corresponding to BPA appears at 0.5 V on Ti/PbO₂ and at 0.3 V on Ti/IrO₂, whereas the oxidation peak is negligible on Ti/SnO₂. It is believed that BPA is not easily oxidized on Ti/SnO₂. These results can be compared to those mentioned in the literature on BPA oxidation with other types of electrodes materials. An oxidation peak of BPA of 1.2 V was recorded by Murugananthan et al. [22] in evaluating the performance of boron-doped diamond, whereas the oxidation peaks using platinum (Pt) and glassy carbon (GC) electrodes were lower than 0.8 V at neutral pH [21–26]. This discrepancy in the oxidation potential peaks can be attributed to the nature and structure of the electrode material. Likewise, from Fig. 2, it can be seen that the Ti/PbO₂ and Ti/IrO₂ anodes had comparable oxygen evolution potentials (1.0 and 1.2 V), whereas the oxygen evolution on Ti/SnO₂ appeared at 1.6 V. The use of anode materials with high oxygen evolution is required for organic

Fig. 2 Cyclic voltammograms recorded for the oxidation of BPA using different anodes (Ti/IrO₂, Ti/SnO₂ and Ti/PbO₂); $[BPA] = 200$ mg l⁻¹; electrolyte $[Na_2SO_4] = 0.1$ M; scan rate = 50 mV s⁻¹; rotating speed = 1,000 rpm

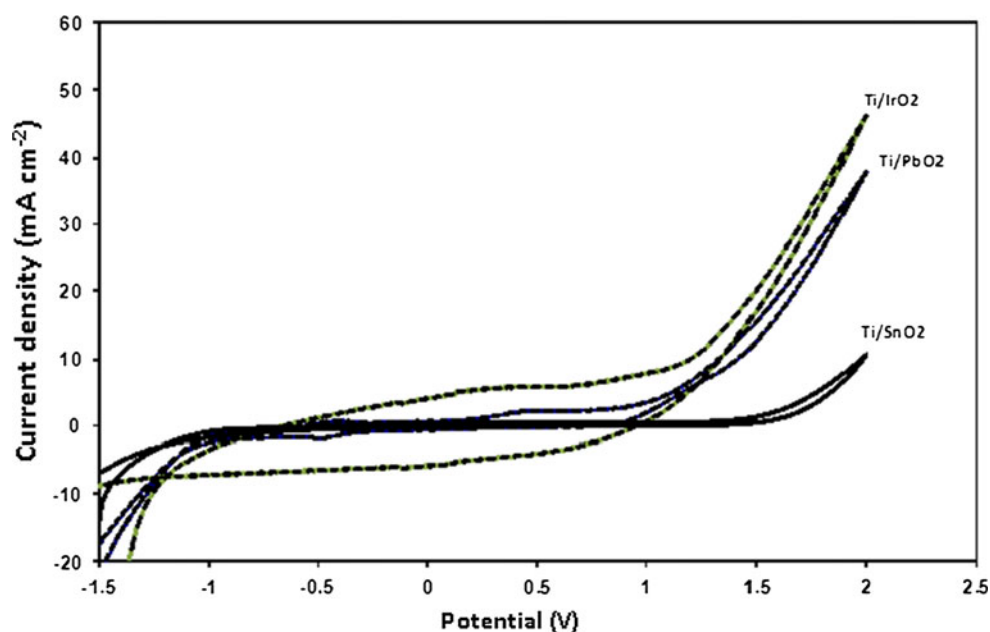
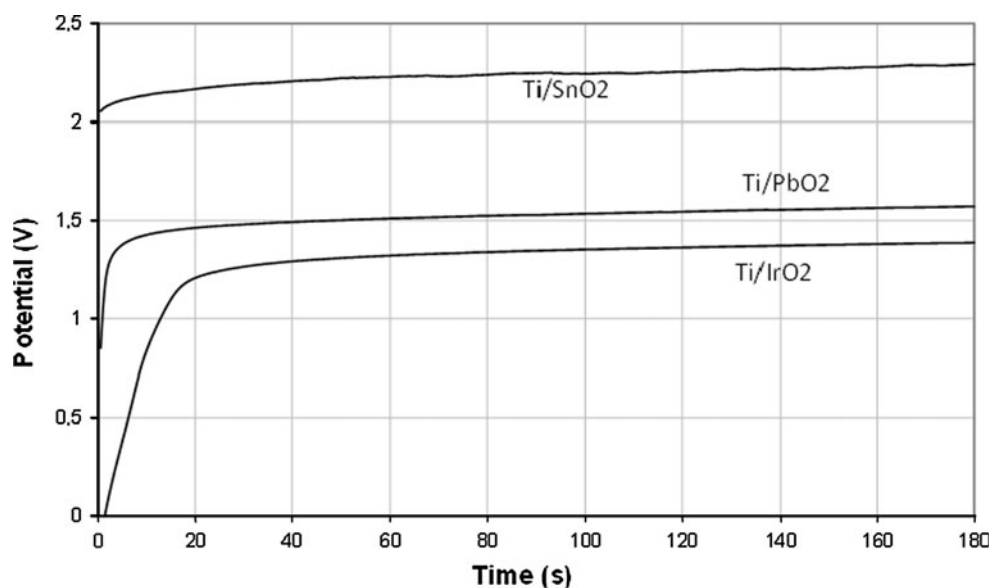


Fig. 3 Chronopotentiometric measurements for the anodic potentials at a current density of 2 mA cm^{-2} using different anodes (Ti/IrO₂, Ti/SnO₂ and Ti/PbO₂); [BPA] = 200 mg l^{-1} ; electrolyte [Na₂SO₄] = 0.1 M ; scan rate = 50 mV s^{-1} ; rotating speed = $1,000 \text{ rpm}$



compound oxidation because oxygen formation does not easily take place on such electrodes [6–27]. Based on this assumption, Ti/SnO₂ seemed to be the best electrode for BPA, but the oxidation peak of BPA was negligible on this electrode compared to Ti/PbO₂. However, it is worth noting that the chemical and crystalline nature of anode electrode can greatly influence both the selectivity and the efficiency of the direct oxidation process [29]. The electrochemical oxidation can be catalyzed by the chemical nature of anode material [16, 29, 30].

Chronopotentiometry was also used to estimate the anodic potentials applied for BPA electrolysis (Fig. 3). A current density of 2 mA cm^{-2} was applied during the tests. The Ti/SnO₂ anode showed the highest potential (2.2 V), followed by Ti/PbO₂ (1.5 V) and Ti/IrO₂ (1.3 V). A higher anodic potential is believed to imply greater energy consumption, which can be unfavorable when increasing the current intensity. Both Ti/PbO₂ and Ti/IrO₂ are more conducive than Ti/SnO₂.

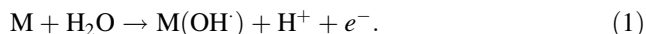
To clearly define the experimental region for the RSM, a preliminary galvanostatic study was performed by separately applying a current intensity of 2.0 A for 40 min

using Ti/SnO₂, Ti/IrO₂ and Ti/PbO₂ anodes. The results are summarized in Table 3. The potential difference existing between the electrodes connected to the power supply increased from 22 V to 36 V using the Ti/SnO₂ anode, whereas it remained constant around 16 V using either the Ti/IrO₂ or Ti/PbO₂ anode. These results are consistent with those previously obtained via chronopotentiometric study. As expected, the energy consumed using Ti/SnO₂ (11.5 kW m^{-3}) was 1.9 times higher than that measured using Ti/IrO₂ or Ti/PbO₂ (6.20 kW m^{-3}). Using Ti/SnO₂, the electrical resistance increased rapidly, indicating that the electrodes were most likely covered with organic substances. A similar behavior has been observed by Nagata et al. [28] in treating different effluents containing endocrine-disrupting chemicals (e.g., 17β -estradiol, bisphenol, pentachlorophenol, and dichlorophenol) using an electro-oxidation process with a three-dimensional electrode system. Nagata et al. [28] analyzed the electrode surface (Ti/Pt anode electrode) before and after the continuous electrochemical process by using X-ray photoelectron spectroscopy (XPS). After the treatment, a large carbon peak was observed instead of the Pt peak, suggesting that the electrode surface was covered with organic substances that were formed during the treatment of the organic-containing effluent. This situation may affect the treatment performance in a long-term experiment. That is why the Ti/SnO₂ was not selected for the next step of the experiments. The comparison between the Ti/IrO₂, Ti/SnO₂ and Ti/PbO₂ anodes showed that Ti/PbO₂ was three times more effective than Ti/IrO₂ and eight times more effective than Ti/SnO₂ for BPA oxidation. In fact, the nature of the electrode material strongly influences both the selectivity and the efficiency of the direct oxidation process. Based on the

Table 3 Data for optimization operation: experimental range and levels of independent process variables using Box–Behnken design

Coded variables (X_i)	Factors (U_i)	Coded levels		
		−1	0	+1
X_1	Current intensity (A)	1.0	2.0	3.0
X_2	Electrolysis time (min)	40	70	100
X_3	Na ₂ SO ₄ conc. (mg l^{-1})	150	200	250

Comminellis model, two types of anodes can be distinguished: *active electrodes* and *non-active electrodes* [29]. In both cases, the first reaction (Eq. 1) occurring in the direct oxidation process is the oxidation of water molecules, which leads to the formation of adsorbed hydroxyl radicals ($\text{OH}\cdot$):



Several authors argue that direct oxidation by Ti/IrO_2 anodes (*active electrode*) occurs through the formation of a higher oxide M-O_{x+1} in the lattice rather than hydroxyl radicals, owing to the higher adsorption enthalpy of the M-OH , where M is the anode electrode [16, 30, 31]. By comparison, on Ti/PbO_2 anodes hydroxyl radicals play an important role due to the weak interaction between the hydroxyl and the electrode surface (*non-active electrode*). As a general rule, the weaker the interaction is, the higher is the anode reactivity for the oxidation of organic compounds. This is one of the reasons why the Ti/PbO_2 anode electrode is more effective for BPA degradation than Ti/IrO_2 .

These results can be compared to the data obtained by Tanaka et al. [21] while treating a synthetic effluent contaminated by BPA with an electrochemical oxidation cell using either a platinum-coated titanium (Ti/Pt) electrode or a tin dioxide-coated titanium (Ti/SnO_2) electrode in the presence of 0.1 M sodium sulfate. The experiments were performed galvanostatically under a constant current at 0.3 A (current density at the anode of 7.96 mA cm^{-2}). It was found that the Ti/SnO_2 anode offered better performance. The complete degradation of 1.0 mM bisphenol-A (228 mg l^{-1} BPA) was achieved at the Ti/SnO_2 anode and the Pt/Ti in 1 and 2 h, respectively. By comparison, in the present study, the preliminary results showed that the Ti/PbO_2 anode offered better performance for BPA degradation in 40 min by imposing a current intensity of 2.0 A (compared to data recorded using Ti/IrO_2 or Ti/SnO_2). The BPA removal yields were 65, 19 and 8.0 % using Ti/PbO_2 , Ti/IrO_2 and Ti/SnO_2 , respectively. The effectiveness of the electro-oxidation process in removing organic compounds depends on the composition of effluent and, more importantly, on the criteria design and operating condition of the electrolytic cell. This discrepancy can be mainly attributed to the design of the electrolytic cell which can greatly influence the mass transfer inside the reactor. In fact, all experiments of Tanaka et al. [21] were carried out using an electrolytic cell (working volume of only 50 ml) equipped with a three-electrode system connected to a potentiostat/galvanostat. The hydrodynamic conditions (mass transfer) can be easily controlled using such an electrolytic system, compared to a two-electrode cell used in the present study. Finally, Ti/PbO_2 anode was selected for the next experiments.

3.2 A BBD for the optimization of BPA degradation during electro-oxidation

In this section, the optimal values of current intensity (U_1 , A), electrolysis time (U_2 , min) and electrolyte concentration (U_3 , mg l^{-1}) for the degradation of BPA were studied. Ti/PbO_2 was used as the anode material. The percentage of BPA degradation (Y_1) and energy consumption (Y_2) were recorded as responses. The data, including natural levels, design, and responses values, are shown in Tables 2 and 4. The factors levels were coded as -1 (low), 0 (central point) and $+1$ (high).

The BDD matrix allows for the description of the region around an optimal response. In our study, it included 12 experiments, where each pair of factors is linked in a 2^2 factorial (assays 1–12). Five additional assays were conducted at the center of the experimental region investigated (assays 13–17). Thus, 17 runs were successively performed, and the percentage of BPA degradation (Y_1) varied from 22 to 97.6%. The regression model in terms of coded variables can be expressed by the following second-order polynomial equation:

$$Y_1 = 71.74 + 20.20X_1 + 15.15X_2 - 0.52X_3 - 0.35X_1X_2 + 6.35X_1X_3 - 0.25X_2X_3 - 10.42X_1^2 - 1.17X_2^2 + 6.9X_3^2 \quad (2)$$

In terms of actual factors, an empirical relation between BPA degradation efficiency (Y_1) and the variables can be expressed by the following second-order polynomial equation:

$$Y_1 = 107.75 + 37.30U_1 + 0.74U_2 - 1.36U_3 - 0.012U_1U_2 + 0.127U_1U_3 - 0.0002U_2U_3 - 10.42U_1^2 - 0.001U_2^2 + 0.003U_3^2 \quad (3)$$

where $1.0 \text{ A} \leq U_1 \leq 3.0 \text{ A}$; $40 \text{ min} \leq U_2 \leq 100 \text{ min}$; $150^\circ\text{mg l}^{-1} \leq U_3 \leq 200^\circ\text{mg l}^{-1}$. The coefficients of the polynomial model (quadratic model) were calculated using the Design-Expert® Program Software. Table 5 shows the analysis of variance (ANOVA) of regression parameters of the predicted response surface quadratic model for BPA removal using an electro-oxidation process. As can be seen from Table 5, the model F value of 79.72 and a low probability value ($\text{Pr} > F = 0.0001$) indicate that the model is significant for BPA removal. The value of the correlation coefficient ($R^2 = 0.990$) indicates that only 1.0% of the total variation could not be explained by the empirical model. According to Joglekar and May [32], R^2 should be at least 0.80 for a good model fit. The R^2 value (0.990) recorded in the present study for BPA removal was higher than 0.80, indicating that the regression model explained the reaction well.

Table 4 Experimental Box–Behnken design and experimental results

Exp. number	Experiment design			Experiment plan			Y ₁ : degradation efficacy (%)	Y ₂ : energy consumption (kW h m ⁻³)
	X ₁	X ₂	X ₃	(A)	Temps (min)	[SO ₄ ²⁻] (mg l ⁻¹)		
1	-1	-1	0	1.0	40	200	22.0	2.11
2	+1	-1	0	3.0	40	200	47.2	13.9
3	-1	+1	0	1.0	100	200	54.2	5.24
4	+1	+1	0	3.0	100	200	97.6	34.0
5	-1	0	-1	1.0	70	150	57.3	4.67
6	+1	0	-1	3.0	70	150	81.3	28.2
7	-1	0	+1	1.0	70	250	42.5	3.47
8	+1	0	+1	3.0	70	250	91.9	21.0
9	0	-1	-1	2.0	40	150	62.7	8.65
10	0	+1	-1	2.0	100	150	92.3	21.0
11	0	-1	+1	2.0	40	250	63.2	6.36
12	0	+1	+1	2.0	100	250	91.8	15.8
13	0	0	0	2.0	70	200	71.6	12.9
14	0	0	0	2.0	70	200	70.0	12.9
15	0	0	0	2.0	70	200	73.2	12.7
16	0	0	0	2.0	70	200	75.1	12.9
17	0	0	0	2.0	70	200	68.8	12.7

Table 5 ANOVA results for the response surface quadratic model for BPA removal and energy consumption

	ANOVA results for BPA removal					
	Model	9	5,901.7	650.75	79.72	<0.0001
	Residual	7	57.58	8.23		
	Lack of fit	3	32.46	10.82	1.72	0.2996
	Pure error	4	25.11	6.28		
	ANOVA results for BPA removal					
	Model	9	4.39	0.48	2,174.62	<0.0001
	Residual	7	1.559×10^{-3}	2.22×10^{-4}		
	Lack of fit	3	1.445×10^{-3}	4.817×10^{-4}	17.71	0.009
	Pure error	4	1.088×10^{-4}	2.720×10^{-5}		

df degree of freedom,
 $R^2 = 0.9903$ (for BPA removal), $R^2 = 0.9996$ (energy consumption)

Regarding energy consumption (Y_2), the regression model in terms of coded variables can also be expressed by the following second-order polynomial equation:

$$Y_2 = 0.77 + 0.61X_1 + 0.34X_2 - 0.12X_3 + 0.25X_1X_2 - 0.09X_1X_3 - 0.043X_2X_3 + 0.073X_1^2 - 0.011X_2^2 + 0.02X_3^2 \quad (4)$$

The analysis of variance (ANOVA) of the regression parameters of the predicted response surface quadratic model for energy consumption shows that the model is significant (F value of 2,174.62 and a low probability value $\text{Pr} > F = 0.0001$). The value of the correlation coefficient ($R^2 = 0.999$) indicates that only 0.1% of the

total variation could not be explained by the empirical model. Three contour plots of constant BPA removal (shown in Fig. 4) are provided to illustrate which combination of factors lead to the high and low oxidation of BPA. The electrolyte concentration was fixed at low, medium, and high levels. It is clear that high rates of BPA removal are recorded with high values of electrolyte concentration, whereas relatively low rate of BPA removal are recorded when one uses medium electrolyte concentrations. In fact, the extremes of high electrolyte concentration, high treatment time, and high current intensity contribute to high BPA oxidation rates, whereas medium electrolyte concentration, low treatment time, and low current intensity result in low BPA oxidation rates.

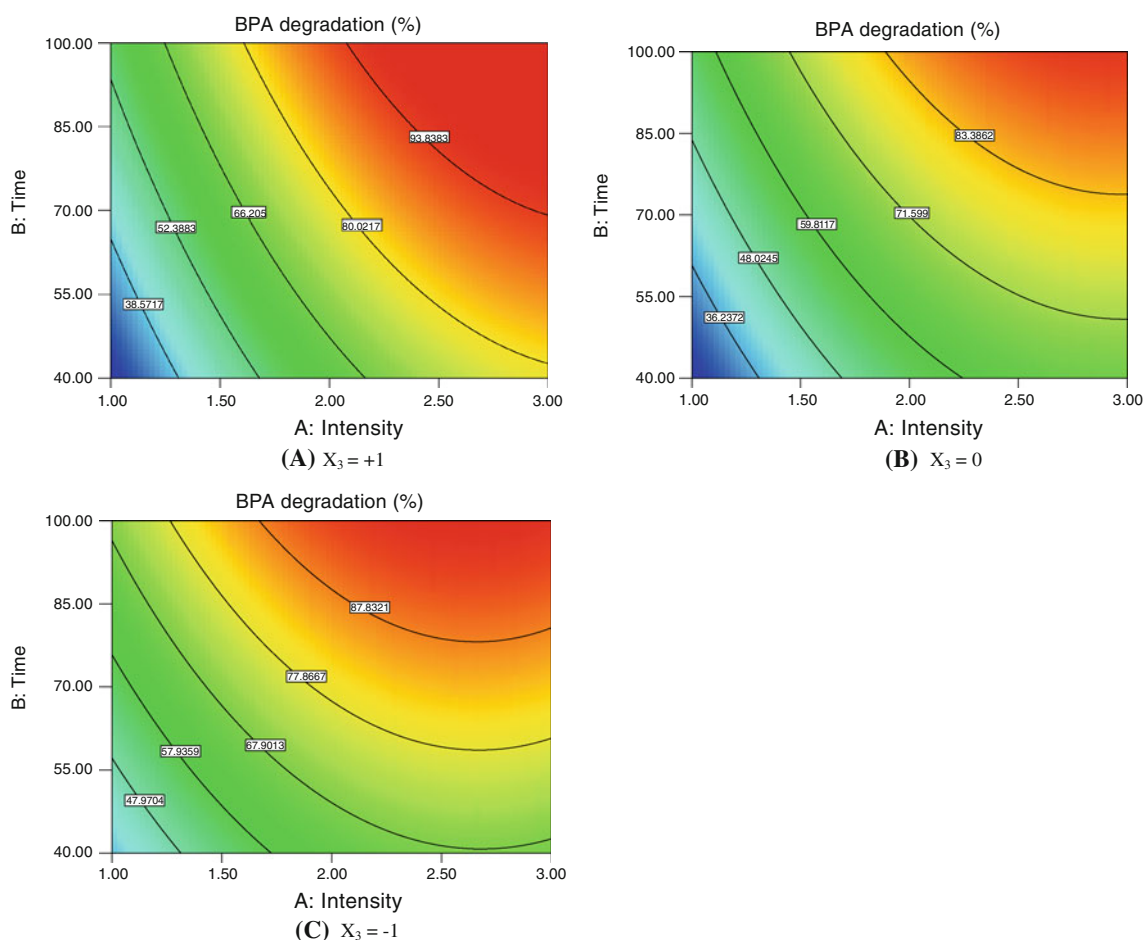


Fig. 4 Contour plots of BPA degradation: **a** electrolyte addition $X_3 = +1$; **b** electrolyte addition $X_3 = 0$; **c** electrolyte addition $X_3 = -1$

To determine the optimal condition for BPA degradation in terms of cost effectiveness, the energy consumption during electrolysis had to be taken into account. The criteria selected for the optimization of BPA degradation are the following: (1) percentage of BPA has to be maximized with (highest importance: 5/5 weighting factor) and (2) energy consumption must be minimized (lower importance: 3/5 weighting factor) to reduce the treatment cost. The treatment costs include energy and electrolyte costs. Based on these criteria, the Design-Expert® Program Software proposed an interesting solution. BPA could be optimally oxidized by up to 90% by applying a current density of 1.94 A and an electrolyte concentration of 250 mg $\text{Na}_2\text{SO}_4 \text{ l}^{-1}$ for a 100-min

reaction period (Table 6). At a cost of 0.060 \$US kW h^{-1} using 0.30-\$US kg^{-1} Na_2SO_4 , the electro-oxidation process involved a total cost of 0.977 \$US per cubic meter of treated effluent. It would be interesting to compare this treatment cost to the costs found in the literature. For instance, the electro-oxidation treatment cost (including only energy and electrolyte cost) was estimated to be 1.32 US\$ m^{-3} by Tran et al. [33] in treating a creosote oily solution (COS) using an electrochemical reactor comprised of rectangular Ti/IrO₂ anodes in the presence of 0.5 g $\text{Na}_2\text{SO}_4 \text{ l}^{-1}$ for a 90-min treatment period. The relatively high treatment cost reported by Tran et al. [33] could be linked to the complexity of the organic pollutant treated (polyaromatic hydrocarbons, PAH).

Table 6 Determination of optimal condition in terms of cost/effectiveness proposed by Design-Expert® Program software

Solution number	Current intensity (A)	Treatment time (min)	Electrolyte concentration (mg l^{-1})	Anode material	Degradation efficacy (%)	Treatment cost ^a (\$ m^{-3})
1	1.94	100	250	PbO ₂	90.13	0.977

^a The treatment cost include only energy and electrolyte consumption cost

3.3 By-product formation and proposed mechanism of BPA degradation

Our intention is to follow the formation of some by-products and possibly identify chemical structures while treating synthetic solutions containing BPA. The electrolysis cell was operated at a current intensity of 2.0 A for 100 min of treatment in the presence of 250 mg $\text{Na}_2\text{SO}_4 \text{ l}^{-1}$ (optimal conditions determined above using the Design-Expert® Program Software). The initial BPA concentration was fixed at 10 mg l^{-1} rather than 1.0 mg l^{-1} to be able to clearly analyze the intermediates using GC–MS. A typical GC pattern of dichloromethane extract containing residual BPA and various reaction intermediates present in the electrolyzed solution after 100 min is shown in Fig. 5 (retention time in the range 5–20 min). Among the peaks observed, some corresponded to single products, whereas others were subjected to interference and required MS identification and monitoring. The analysis of the electrolyzed solution shows several peaks [(A), (B), (C), (D), (E), (F) and (BPA) peaks] identified in the gas chromatogram, which were analyzed in detail via mass spectroscopy (Fig. 6). Components (A), (B), (C), (D), (F) and (F) corresponded to methoxyphenol, maleic acid, hydroquinone, hydroxyacetophenone, hydroxymethylphenol and biphenyldiol, respectively (by comparing their mass spectra with those of the NIST mass spectra library) (Table 7). It may be interesting to compare these intermediates with those found in the literature for the degradation of BPA under various experimental conditions. For instance, Murugananthan et al. [22] identified principally phenol, benzoquinone and hydroquinone during the electro-oxidation of BPA using a boron-doped diamond (BDD) electrode. Aromatic compounds (benzoquinone,

hydroquinone and hydroxylated BPA) and aliphatic compounds (maleic acid) were identified by Cui et al. [6] in treating a synthetic solution containing BPA using different anode materials (Ti/BDD, Ti/Sb– SnO_2 , Ti/RuO₂ and Pt).

Inoue et al. [34] recorded some aromatic intermediates (such as 3-hydroxybisphenol-A, methylethenylphenol, hydroquinone and benzoquinone, etc.) and aliphatic intermediates (such as formaldehyde and organic acids) while using ultrasonication at a frequency of 404 kHz and intensities varying from 3.5 to 12 kW m^{-2} . Most of these intermediates found in the literature were identified in the present study.

Based on the primary intermediates found, the reaction pathways of BPA degradation can be proposed (Fig. 7). First (pathway I), hydroxyl radicals produced on the anode electrode react with BPA by electrophilically attacking the aromatic ring and lead to the formation of hydroxylated derivatives of BPA (ortho-hydroxylated BPA and para-hydroxylated BPA) [6]. Ortho- and para-hydroxylated compounds can be consecutively transformed via the following attack by hydroxyl radicals into further intermediates and lead to the formation of catechol, methylethenylphenol and hydroquinone (C). The subsequent oxidation of hydroquinone may result in the formation of benzoquinone, followed by the formation of open-ring structures, such as maleic acid (B). The oxidation of maleic acid may result in fully oxidized reaction products and leads to the formation of carbon dioxide (CO_2). This hypothesized CO_2 formation is based on results described elsewhere [33] for the treatment of a synthetic solution containing various concentrations of polycyclic aromatic hydrocarbons (PAH). The yields of COD and TOC removal were 62 and 27%, respectively.

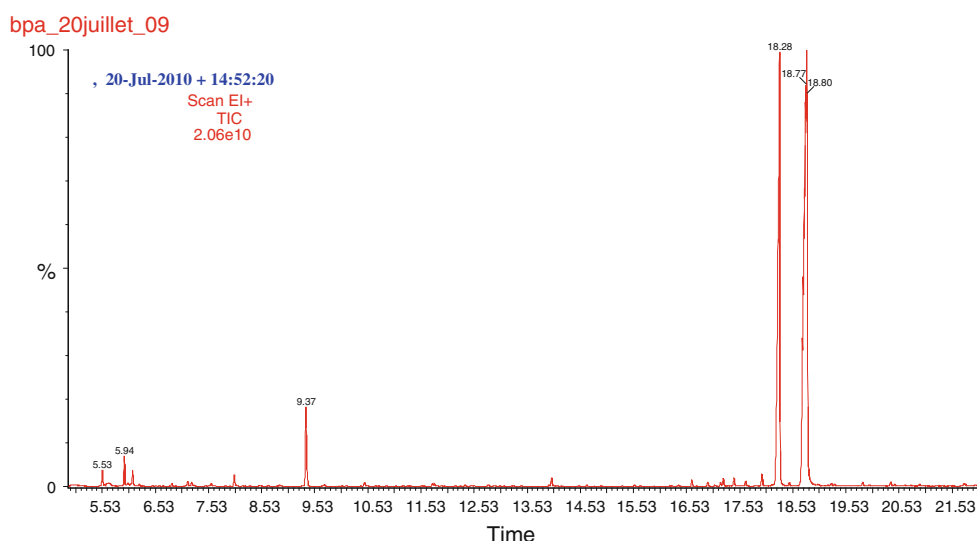


Fig. 5 Chromatograph extracts obtained after 100 min of BPA electro-oxidation. Current intensity = 2.0 A; $[\text{Na}_2\text{SO}_4] = 250 \text{ mg l}^{-1}$; anode electrode Ti/PbO₂

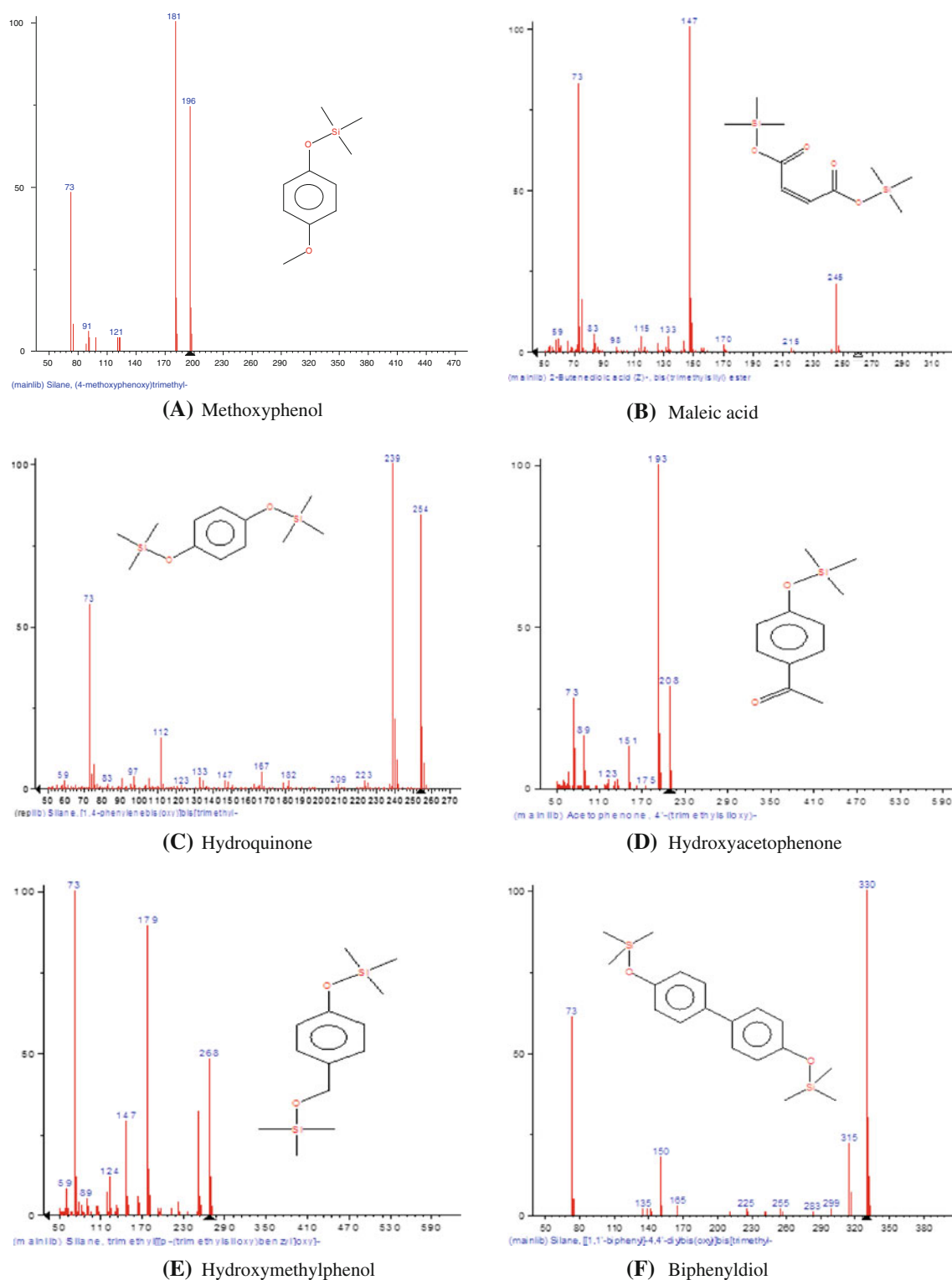


Fig. 6 Mass spectra of components **a–f** produced by BPA electro-oxidation

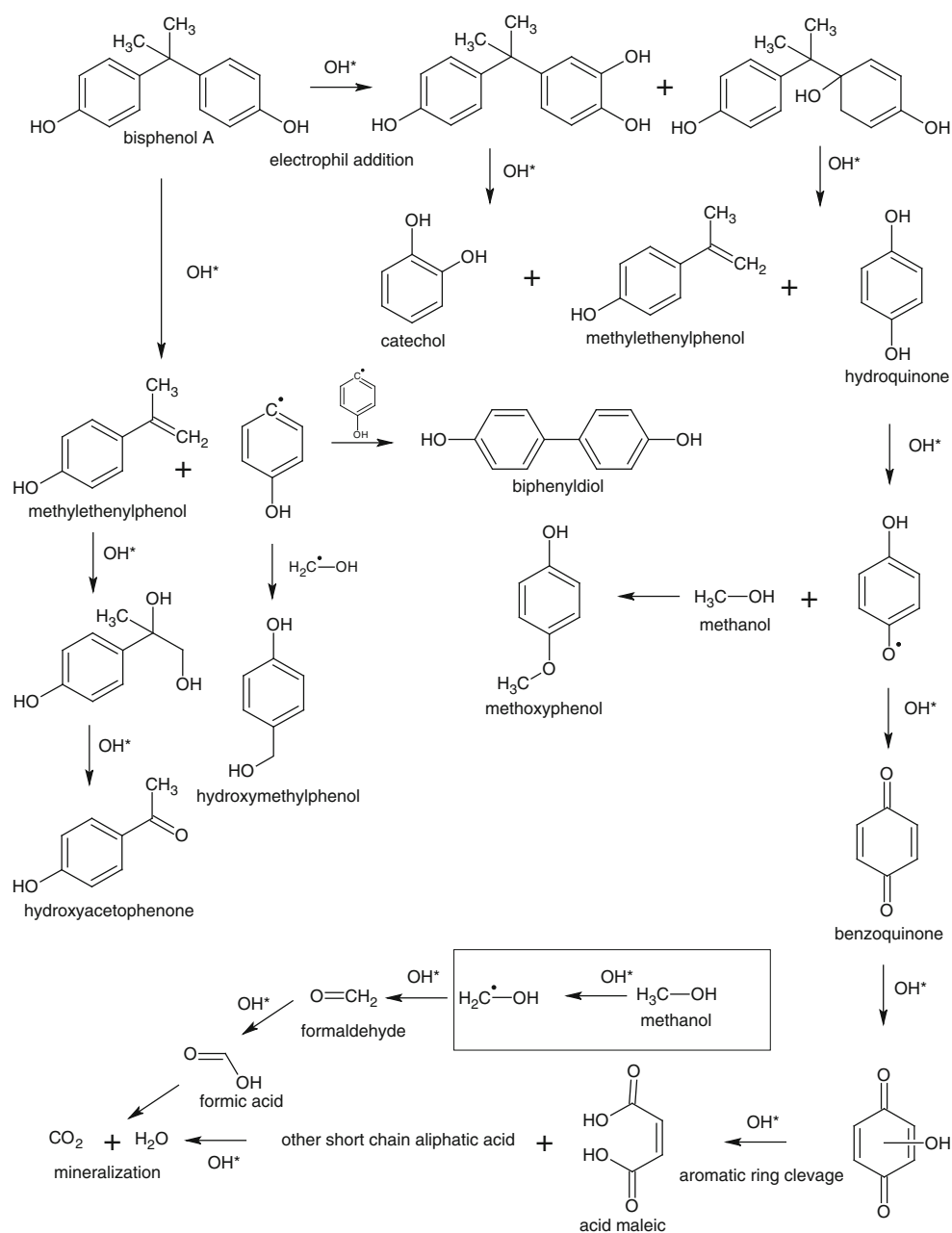
The relatively low yield of TOC removal (27%), as compared to 62% of COD removal, indicated that only a small fraction of PAH was completely oxidized into water and carbon dioxide, the majority of the pollutants being

transformed into small molecules that reduced the oxygen demand in the treated solution.

Another pathway (pathway II) of BPA degradation proposed in Fig. 7 is based on the possibility of forming

Table 7 By-products of BPA electro-oxidation identified by GC–MS

Product	RT ^a	Fragment (<i>m/z</i>)	Peaks	Peak surface ($\times 10^6$)
Methoxyphenol (TMS)	6.84	196[M] ⁺ , 181[M-Met] ⁺	A	3.42
Maleic acid (TMS)	8.02	245[M-Met] ⁺ , 147[DMSOTMS] ⁺	B	14.79
Hydroquinone (TMS)	9.37	254[M] ⁺ , 239[M-Met] ⁺	C	96.45
Hydroxyacetophenone (TMS)	10.29	208[M] ⁺ , 193[M-Met] ⁺	D	0.38
Hydroxymethylphenol (TMS)	10.68	268[M] ⁺ , 179[M-OTMS] ⁺	E	0.55
Biphenyldiol (TMS)	17.64	330[M] ⁺ , 150[M-phOTMS] ⁺	F	6.71
Bisphenol-A (TMS)	18.28	372[M] ⁺ , 357[M-Met] ⁺ , 207[M-ph-OTMS] ⁺	BPA	886

^a Retention time (min)**Fig. 7** Proposed reaction mechanisms for the anodic oxidation of BPA with Ti/PbO₂ electrode

methylethenylphenol (A) during electrolysis, which can successively react with hydroxyl radicals to form hydroxyacetophenone (D). The formation of biphenyldiol (F) can result from the reaction between two intermediates of phenol, whereas the formation of hydroxymethylphenol (E) can result from the reaction between phenol and methanol. It is worth noting that methanol was added during the preparation of synthetic BPA solution.

3.4 Application to wastewater treatment contaminated by BPA

The effectiveness of the electrolytic cell in treating wastewater effluent contaminated by BPA (around 1.0 mg l^{-1}) was evaluated at a current intensity of 2.0 A Ti/PbO₂ anode electrode and a retention time of 100 min (optimal condition determined above using the Design-Expert® Program Software) were used but without the addition of the electrolyte (Na₂SO₄). The objective was to test the effectiveness of the electrolytic cell as a tertiary treatment to remove emerging pollutants such as BPA. It was important to determine whether the results of these tests are reproducible or not. To that end, the experiments were repeated in triplicate to verify the effectiveness and reproducibility of electro-oxidation performance in treating municipal wastewater effluent (MWE) contaminated by BPA. Table 8 compares the untreated (raw water and control sample) and the MWE treated by electro-oxidation. The raw effluent was the initial MWE to which $1.0 \text{ mg BPA l}^{-1}$ was added. The control assay consisted only of recirculating the MWE in the electrolytic cell without imposing any current intensity during a period of 100 min . It is important to underline the fact that the raw effluent contained $465 \pm 20 \text{ mg Cl}^{-} \text{ l}^{-1}$, which facilitated the passage of electrical current. Moreover, these ions favored hypochlorous acid (HClO) production and thus improved BPA oxidation. The increase in the oxidation–

reduction potential (ORP) from $180 \pm 30 \text{ mV}$ (measured in the raw effluent) to $379 \pm 34 \text{ mV}$ (recorded in the electrolyzed effluent) was mainly due to HClO generation ($0.226 \pm 0.060 \text{ mM}$). The yields of BPA removal were determined by subtracting the residual BPA concentration from the initial value recorded in MWE, and the resulting value was divided by the same initial concentration of BPA. A concentration of $0.93 \pm 0.2 \text{ mg BPA l}^{-1}$ was measured in the initial MWE. A concentration of $0.84 \pm 0.02 \text{ mg BPA l}^{-1}$ was recorded in the control assay, which corresponded to an abatement of 9.7% . The decrease in BPA concentration during the control assay was attributed to the volatilization of the fraction of BPA or adsorption of BPA on the electrodes or on the pipe of the experimental unit. Under an applied current intensity, the degradation of BPA increased to more than 99.9% . The residual concentration of BPA was below the detection limit (i.e., $<0.005 \text{ mg BPA l}^{-1}$). Considering possible volatilization and adsorption, BPA degradation can be obtained by subtracting the yields of BPA removal (while imposing current intensity) from the yields recorded without applied current intensity. Thus, under our experimental conditions, the real rate of BPA degradation was around 90% . It is worth noting that 30 min of electrolysis was sufficient to reach complete BPA degradation even if the total treatment period was 100 min . In fact, under our experimental conditions using MWE, BPA can be oxidized by both direct anodic electrochemical oxidation (by means of OH·) and indirect electrochemical oxidation via mediators, such as hypochlorous acid generated by chloride oxidation. Both actions (direct and indirect effects) lead to the formation of powerful oxidizing agents capable of rapidly oxidizing the BPA. The combination of both effects accelerates BPA degradation. Similar results have been recorded by Panizza et al. [11] in treating real chemical wastewater containing naphthalene- and anthraquinone sulfonic by combining direct and indirect electro-oxidation.

Table 8 Application to municipal wastewater effluent contaminated by BPA ($1.0 \text{ } \mu\text{g l}^{-1}$)

Parameters	Untreated effluent		Treated effluent
	Raw effluent	Control	
Current intensity (A)	0.00 ± 00	0.00 ± 00	2.0 ± 0.0
Potential (V)	0.00 ± 00	0.00 ± 00	7.9 ± 0.1
Conductivity ($\mu\text{S cm}^{-1}$)	$1,859 \pm 31$	$1,781 \pm 28$	$1,656 \pm 42$
Energy (kW h m^{-3})	0.00 ± 00	0.00 ± 00	0.026 ± 00
POR (mV)	180 ± 30	180 ± 30	379 ± 34
pH	7.74 ± 0.13	7.99 ± 0.25	7.97 ± 0.18
Cl^{-} (mg l^{-1})	465 ± 20	441 ± 7	410 ± 11
HClO (mM)	0.0 ± 0.0	0.0 ± 0.0	0.226 ± 0.057
Turbidity (NTU)	3.72	3.72	3.75
Residual BPA (mg l^{-1})	0.93 ± 0.20	0.84 ± 0.02	<0.005
BPA removal (%)	–	9.7	>99.9

Table 9 Concentration ($\mu\text{g l}^{-1}$) of trihalomethanes (THMs), aliphatic halogenated hydrocarbon (AHH), monocyclic aromatic hydrocarbons (AMHs) in the effluent samples from untreated and treated municipal effluent measured during the application of optimal conditions

Organic pollutants	Untreated effluent	Treated effluent	Detection limits	Permissive level ^a
Trihalomethanes (THMs)				
Chloroform	3.2 ± 0.8	31.0 ± 2.0	<0.1	–
Dibromochloromethane	1.1 ± 0.2	2.1 ± 0.0	<0.1	–
Bromodichloromethane	0.2 ± 0.5	2.8 ± 0.3	<0.1	–
Bromoform	<0.1	<0.1	<0.1	–
Total THMs	4.5	35.9	–	100
Aliphatic halogenated hydrocarbon (AHH)				
Dichloromethane	1.1 ± 0.2	2.1 ± 0.0	<0.9	50
Carbon tetrachloride	<0.1	<0.1	<0.1	5.0
1,1,2,2-Tetrachloroethane	<0.1	<0.1	<0.1	–
Vinyl chloride	<0.2	<0.2	<0.2	2.0
Trichloroethylene	0.7 ± 0.6	3.4 ± 0.6	<0.1	50
Tetrachloroethylene	0.4 ± 0.3	1.4 ± 0.1	<0.1	30
Aromatic monocyclic hydrocarbons (AMHs)				
Benzene	<0.2	<0.2	<0.2	5
Toluene	<0.1	<0.1	<0.1	24
Chlorobenzene	<0.1	<0.1	<0.1	–
Ethylbenzene	<0.1	<0.1	<0.1	2.4
Styrene	<0.1	<0.1	<0.1	–
1,3,5-Trimethylbenzene	<0.1	<0.1	<0.1	–
1,2,4-Trimethylbenzene	<0.1	0.1 ± 0.1	<0.1	–
1,3-Dichlorobenzene	<0.1	<0.1	<0.1	200
1,4-Dichlorobenzene	<0.1	<0.1	<0.1	5.0

^a Permissive level for drinking water quality (Government of Canada, 2010)

Three types of anodes were used (Ti/Pt, Ti–Ru–Sn–SbO₂ and carbon felt) either in the presence of a supporting electrolyte NaCl (1.0–10 g l^{−1}) or without the addition of electrolyte at a current density of 50 mA cm^{−2}. It was found that the Ti/Pt anodes offered better performance in the presence of 5.0 g NaCl l^{−1}. For instance, approximately 67% of COD was removed at 7.0 Ah l^{−1}, whereas only 40% of COD was reduced without the addition of an electrolyte.

The toxic organic contaminants in the treated MWE were analyzed and compared with those measured in the untreated effluent. The main organic contaminants found in MWE are summarized in Table 9. These toxic organics include trihalomethane (THMs), aliphatic halogenated hydrocarbons (AHHs) and AMHs. The residual concentrations measured (in treated and untreated effluent) were compared to those recommended by the Government of Canada for drinking water. Because the guidelines for Quebec City regarding effluent discharge (containing toxic organics) in sewage urban works are not clearly established, we decided to compare the concentrations of residual THMs, AHHs and AMHs with those recommended for drinking water quality, which are well established. The AMH concentrations measured in both the treated and untreated effluent were mostly below

0.1–0.2 $\mu\text{g l}^{-1}$ or below the detection limit. The total THMs (chloroform, dibromochloromethane, bromodichloromethane and bromoform) measured in the untreated effluent was 4.53 $\mu\text{g l}^{-1}$. In comparison, 38.8 $\mu\text{g l}^{-1}$ of total THMs was recorded in the treated effluent (an increase of 87% of THMs). However, this residual concentration recorded for the treated effluent was below the level (100 $\mu\text{g l}^{-1}$) recommended by the Government of Canada for drinking water. The AHH concentrations measured in both the treated and untreated effluent were mostly below 4.0 $\mu\text{g l}^{-1}$ or below the detection limit. Again, it is worth noting that all residual concentrations of AHHs in the treated effluent were below the values recommended for drinking water. Because the acceptable levels recommended for drinking water are generally more restrictive than those for wastewater discharge, we can conclude that the treated effluent was of sufficient quality to be rejected in the receiving water.

4 Conclusion

The electro-oxidation of BPA was tested using three different anode materials: Ti/SnO₂, Ti/IrO₂ and Ti/PbO₂. The first part of this study was performed in synthetic

media using only sodium sulfate as an electrolyte; thus, only the contribution of the direct effect of electrolysis was taken as evidence. The best results for BPA degradation were obtained with the Ti/PbO₂ anode. An experimental design methodology (2³ BBD) was applied to determine the optimal experimental conditions in terms of cost effectiveness. The best conditions were found to be 100 min of electrolysis with Ti/PbO₂ operated with a current intensity of 2 A in the presence of 250 ppm of sodium sulfate. Under these conditions, 91% of BPA abatement could be achieved at an operating cost of 0.977 \$ m⁻³. Based on the primary intermediates identified, reaction pathways of BPA degradation were proposed. The principal pathway of degradation corresponded first to the attack by hydroxyl radicals to form unstable hydroxylated BPA derivatives, which led to the formation of aromatic-ring compounds. The subsequent oxidation of these aromatic compounds led to the formation of opening structures and aliphatic acid. A comparison of the results obtained from the degradation of BPA in synthetic solution and those obtained in real wastewater artificially doped with BPA were conducted to evaluate the effect of the matrix and eventual competition with organic matter. The results indicate that the degradation of BPA is much more efficient in real wastewater than in synthetic solution due to the presence of a high concentration of chloride ions that could easily be transformed into active chlorine. In view of describing well the polymeric film deposited on anode electrode, analysis of electrode surface before and after the treatment should be carried out using either X-ray photoelectron spectrometry (XPS), scanning force microscopy (SFM) or X-ray diffraction (XRD) technique.

Acknowledgments Sincere thanks are extended to the National Sciences and Engineering Research Council of Canada for their financial contribution to this study.

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